PB84-100130

# Effects of Selected Inorganic Coal-Gasification Constituents on Aquatic Life: An Annotated Bibliography

Tennessee Valley Authority, Muscle Shoals, AL
Office of Natural Resources

Mar 83

U.S. Department of Commerce
National Technical Information Service
NTIS

TVA

EPA

Tennessee Valley Authority
Office of Natural Resources
Muscle Shoals AL 35660

PB84-100130

United States Environmental Protection Agency
Office of Environmental Processes and Effects Research
Washington DC 20460

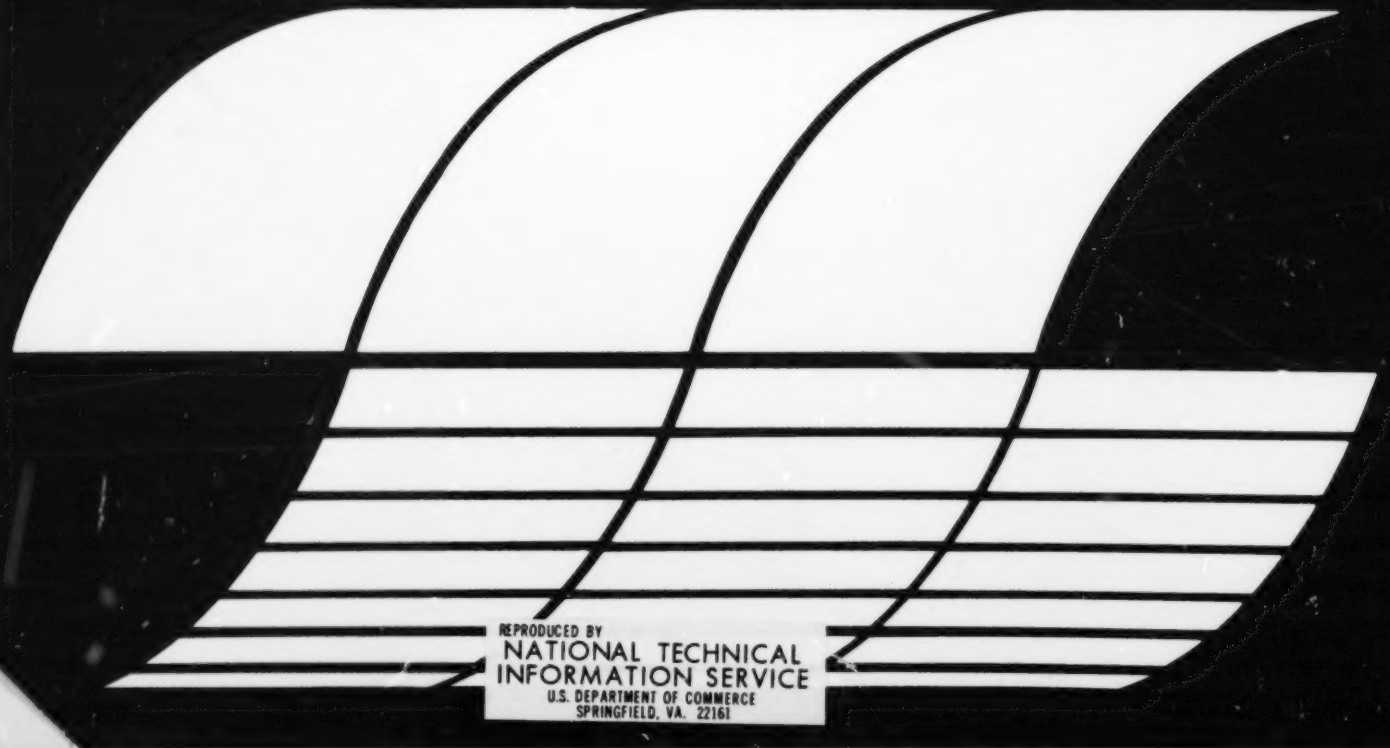
EPA 600 7 83 018
March 1983

Research and Development

# Effects of Selected Inorganic Coal-Gasification Constituents on Aquatic Life:

## An Annotated Bibliography

## Interagency Energy/Environment R&D Program Report



REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

| TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing) | | |
|---|---|---|
| 1. REPORT NO. EPA-600/7-83-018 | 2. | 3. RECIPIENT'S ACCESSION NO. PB84 100130 |
| 4. TITLE AND SUBTITLE EFFECTS OF SELECTED INORGANIC COAL-GASIFICATION CONSTITUENTS ON AQUATIC LIFE: AN ANNOTATED BIBLIOGRAPHY | | 5. REPORT DATE March 1983<br>6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) Leroy M. Koch and Richard C. Young | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS<br>Office of Natural Resources<br>Division of Water Resources<br>Tennessee Valley Authority<br>Muscle Shoals, AL 35660 | | 10. PROGRAM ELEMENT NO. CC2NIA<br>11. CONTRACT/GRANT NO. IAG EPA-IAG-79-0-X0511 |
| 12. SPONSORING AGENCY NAME AND ADDRESS<br>U.S. Environmental Protection Agency<br>Office of Research & Development<br>Office of Environmental Processes & Effects Res.<br>Washington, DC 20460 | | 13. TYPE OF REPORT AND PERIOD COVERED<br>14. SPONSORING AGENCY CODE EPA/600/16 |
| 15. SUPPLEMENTARY NOTES | | |


16. ABSTRACT

This review is concentrated on primary inorganic pollutants of concern which result in the aqueous discharges of high-pressure coal-gasification technologies. These pollutants include ammonia, cyanide (thiocyanates), sulfide, and boron. Ammonia toxicity was not reviewed since effective waste treatment technologies and discharge guidelines are available.

The open literature concerning the effects of cyanide (thiocyanates), boron, and sulfide on aquatic life was reviewed using computer search techniques to obtain information from the Department of Energy RECON data base, the BIOSIS biological file in ORBIT data base, chemical abstracts, and the National Technical Information Service.

It was concluded that there is a void in the literature concerning the toxicity of these parameters in high-pressure, coal-gasification wastewater matrices. The information abstracted is mainly concerned with laboratory studies with individual constituents; however, some data provide insight to the effects of physical parameters such as temperature and physical stress.


| 17. KEY WORDS AND DOCUMENT ANALYSIS | | | |
|---|---|---|---|
| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| Coal gasification<br>Toxicity<br>Teratogenesis<br>Aquatic Organisms<br>Fishes<br>Algae<br>Daphnia pulex | Cyanide<br>Thiocyanates<br>Sulfide<br>Sulfite<br>Boron | Fuel Extraction<br>Transport and Fate<br>Ecological Effects<br>Synthetic Fuels | 6F<br>10A |
| 18. DISTRIBUTION STATEMENT | | 19. SECURITY CLASS (This Report) Unclassified | 21. NO. OF PAGES 39 |
| | | 20. SECURITY CLASS (This page) Unclassified | 22. PRICE |

EPA Form 2220-1 (9-73)

EPA-600/7-83-018
March 1983

# EFFECTS OF SELECTED INORGANIC COAL-GASIFICATION CONSTITUENTS ON AQUATIC LIFE: AN ANNOTATED BIBLIOGRAPHY

Prepared by

Leroy M. Koch

Principal Investigator
Richard C. Young

Office of Natural Resources
Division of Water Resources
Fisheries & Aquatic Ecology Branch
Tennessee Valley Authority
Muscle Shoals, Alabama 35660

Interagency Agreement No. EPA-IAG-79-0-X0511
Project No. 82 BDW
Program Element No. CC2N1A

Project Officer

Alan Moghissi
Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

Prepared for

OFFICE OF ENVIRONMENTAL PROCESSES AND EFFECTS RESEARCH
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460

## DISCLAIMER

This report was prepared by the Tennessee Valley Authority and has been reviewed by the Office of Research and Development, Energy and Air Division, U.S. Environmental Protection Agency, and approved for publication. Although the research described in this document has been funded wholly or in part by the United States Environmental Protection Agency through Interagency Agreement No. EPA-IAG-79-D-X0511 with TVA, it has not been subject to Agency policy and peer review and therefore does not necessarily reflect the views of the agency or the Tennessee Valley Authority and no official endorsement should be inferred.

## ABSTRACT

This review is concentrated on primary inorganic pollutants of concern which result in the aqueous discharges of high-pressure coal-gasification technologies. These pollutants include ammonia, cyanide (thiocyanates), sulfide, and boron. Ammonia toxicity was not reviewed since effective waste treatment technologies and discharge guidelines are available.

The open literature concerning the effects of cyanide (thiocyanates), boron, and sulfide on aquatic life was reviewed using computer search techniques to obtain information from the Department of Energy RECON data base, the BIOSIS biological file in ORBIT data base, chemical abstracts, and the National Technical Information Service. Key words used included coal gasification, toxicity, teratogenesis, aquatic organisms, fishes, algae, Daphnia pulex, cyanide, thiocyanates, sulfide, sulfite, and boron.

It was concluded that there is a void in the literature concerning the toxicity of these parameters in high-pressure, coal-gasification wastewater matrices. The information abstracted is mainly concerned with laboratory studies with individual constituents; however, some data provide insight to the effects of physical parameters such as temperature and physical stress.

## ACKNOWLEDGEMENTS

This work was conducted as part of the Federal Interagency Energy/ Environment Research and Development Program with funds administered through the Environmental Protection Agency (EPA Contract No. 79-D-X0511).

The EPA Project Officer for the project is Alan Moghissi, and the TVA Project Director is Billy G. Isom, E&D Building, Muscle Shoals, Alabama.

CONTENTS


| | Page |
|---|---|
| Abstract | iii |
| Acknowledgement | iv |
| CYANIDE | 1 |
| Fish | 2 |
| Eggs and Hatching | 2 |
| Sac Fry | 2 |
| Juvenile | 3 |
| Adults | 3 |
| Physiology | 7 |
| Behavior | 9 |
| Bioconcentration | 9 |
| Invertebrates | 10 |
| Acute Effects | 10 |
| BORON | 11 |
| Fish | 12 |
| Acute and Chronic | 12 |
| Invertebrates | 15 |
| Acute | 15 |
| Aquatic Plants | 16 |
| Microorganisms | 16 |
| SULFIDE | 17 |
| Fish | 18 |
| Eggs and Hatching | 18 |
| Sac Fry | 19 |
| Juvenile - Adults | 20 |
| Chronic Tests - Fish-Bluegills | 21 |
| Physiology | 26 |
| Invertebrates | 30 |
| Acute and Chronic | 30 |

# CYANIDE

## FISH

## (ACUTE AND CHRONIC)

### EGGS AND HATCHING

Lind, David T., Lloyd L. Smith, Jr., and Steven J. Broderius. 1977. Chronic effects of hydrogen cyanide on the fathead minnow. Journal WPCF, 49:262-268.

Lind et al. (1977) found the number of eggs produced by female fathead minnows was significantly reduced at concentrations of 0.0196 mg/l HCN and above.

Leduc, Gerard. 1978. Deleterious effects of cyanide on early life stages of Atlantic salmon (Salmo salar). Journ. Fish. Res. Bd. Canada, 35:166-174.

Leduc (1978) found continuous exposure of Atlantic salmon eggs to cyanide in a range of 0.01-0.10 mg/l HCN caused hatching failures of about 15 to 40%.

Leduc (1978). Hatching was delayed 6-9 days at cyanide concentrations of 0.08 and 0.10 mg/l HCN; water temperature was 5.4°C. Hatching was not delayed at lower concentrations of HCN.

Lind, David T., Lloyd L. Smith, Jr., and Steven J. Broderius. 1977. Chronic effects of hydrogen cyanide on the fathead minnow. Journal WPCF, 49:262-268.

Lind et al. (1977) estimated that the highest no-effect level of hydrogen cyanide for the fathead minnow lies between 0.0129 and 0.0196 mg/l based on statistical evaluation of egg production.

### SAC FRY - JUST AFTER HATCHING

Leduc, Gerard. 1978. Deleterious effects of cyanide on early life stages of Atlantic salmon (Salmo salar). Journ. Fish. Res. Bd. Canada, 35:166-174.

Leduc (1978) determined cyanide had no apparent effect on survival of Atlantic salmon sac fry after hatching, but markedly affected growth-producing fry that were 10% shorter than controls at concentrations of 0.04 mg/l HCN and greater.

Leduc (1978) noticed in Atlantic salmon fry an accelerated increase in body length after hatching in low concentrations of cyanide.

In 0.08 and 0.10 mg/l HCN, 58 days after hatching, the fry, initially smaller than the controls, were equal to if not longer than the controls. In addition, those fry exposed to intermediate concentrations were longer than the controls. Increase in weight essentially paralleled the observations of increase in length.

Leduc (1978) found, during the posthatching period, abnormal Atlantic salmon fry were present with observable defects including malformation and/or absence of the eyes, defects in mouth and vertebral column, and yolk-sac dropsy (hydrocoele embryonalis).

Leduc (1978) showed a high incidence of abnormalities in Atlantic salmon ranging from about 6% at 0.01 mg/l to about 19% at 0.10 mg/l HCN at a water temperature of 4.4°C.

Lind, David T., Lloyd L. Smith, Jr., and Steven J. Broderius. 1977. Chronic effects of hydrogen cyanide on the fathead minnow. Journal WPCF, 49:262-268.

Lind et al. (1977) found that fry exposed to treatment levels of 34.8 µg/l HCN and above after 28 days were significantly shorter than control fish. In one treatment level below 34.8 µg/l HCN at 26.3 µg/l HCN, fish were significantly longer than controls.

Lind et al. (1977) found that fathead minnow fry in treatment experiments with HCN after 28 and 56 days tended to approach the same size of control fish.

JUVENILE

Lind, David T., Lloyd L. Smith, Jr., and Steven J. Broderius. 1977. Chronic effects of hydrogen cyanide on the fathead minnow. Journal WPCF, 49:262-268.

Lind et al. (1977) determined that the lethal threshold concentration of hydrogen cyanide for juvenile fathead minnows at 25°C, pH 8, and 6 mg/l DO, derived from acute toxicity bioassays, is approximately 0.012 mg/l.

ADULTS

Shelford, Victor E. 1917. An experimental study of the effects of gas waste upon fishes, with especial reference to stream pollution. Bull. Illinois State Laboratory Nat. History, Vol. XI, Article VI, pp. 395-398.

Shelford (1917) found when Lepomis humilus were exposed to a concentration of 0.280-0.300 grams of ammonium sulphocyanate ($NH_4$)

(280-300 ppm) and a concentration of ammonium ferrocyanide $(NH_4)_4$, 0.150-0.200 gm (150-200 ppm) spasms were common before death which occurred in one hour at a temperature of 20°C.

Herbert, D.W.M. and J. C. Merkens. 1952. The toxicity of potassium cyanide to trout. Jour. Exp. Bio., 29:632-649.

Herbert and Merkens (1952) showed in experiments with one-year-old rainbow trout, ranging in length from 5.5 to 17.5 cm in dynamic bioassays, water temperature 17.5, with a concentration of 0.153 ppm CN, that longer fish usually succumbed sooner than shorter fish.

Doudoroff, Peter, Gerard Leduc, and Carl R. Schneider. 1966. Acute toxicity to fish of solutions containing complex metal cyanides, in relation to concentrations of molecular hydrocyanic acid. Trans. Amer. Fish. Soc., 95:6-22.

Doudoroff et al. (1966) determined in tests of continually renewed NaCN solutions at 20°C, with a pH of 7.8 to 7.9, that free cyanide concentrations near and below 0.15 mg/l as HCN could be tolerated by most of the bluegills tested indefinitely.

Doudoroff et al. (1966). The median tolerance limits ($TL_m$) for bluegill is about 0.14 or 0.15 mg/l of molecular HCN with a pH of 7.85. Lower concentrations were indefinitely tolerable for bluegill under test conditions.

Broderius, Steven J. and Lloyd L. Smith, Jr. 1979. Lethal and sublethal effects of binary mixtures of cyanide and hexavalent chromium, zinc, or ammonia to the fathead minnow (Pimephales promelas) and rainbow trout (Salmo gairdneri). Journ. Fish. Res. Bd. Canada, 36:164-172.

Broderius and Smith (1979) determined the 96-hour $LC_{50}$ of HCN to fathead minnows and rainbow trout to be 0.125 and 0.057 mg/l, respectively. Water temperature for the minnows was 25°C and 10°C for the trout, while pH was 7.8 for the minnow tests and 7.95 for the trout.

Broderius and Smith (1979) determined 96-hour $LC_{50}$s, in water with temperature and pH as above, for fathead minnows in Cr-HCN to be 1.31 toxic units and to rainbow trout of $NH_3$-HCN to be 0.859 toxic units.

Broderius and Smith (1979). In 30-day tests on fathead minnows with Zn at 0.76 and 0.84 mg/l and those with a mixture of HCN and Zn at 0.045 and 0.62 and 0.057 and 0.86 mg/l, respectively, survival was about 65% and 40% of that in the controls, respectively.

Broderius and Smith (1979). Rainbow trout were markedly affected by 0.044 mg/l HCN with survival after 30-day exposure being 30% of that in the controls.

Burdick, George Edgar and Morris Lipschuety. 1948. Toxicity of ferro- and ferricyanide solutions to fish and determination of the cause of mortality. Trans. Amer. Fish. Soc., 78:192-202.

Burdick and Lipschuety (1948) found that a cyanide concentration of approximately 0.19 ppm was toxic in laboratory tests to Rhinichthys atratulus and Semotilus atromaculatus atromaculatus, and at which level 100% mortality occurred within 76 hours and 50% mortality within 48 hours.

Burdick and Lipschuety (1948) showed that potassium ferro- and ferricyanide solutions in concentrations as low as 2 ppm are toxic to fish life in the presence of sunlight.

Downing, Kathleen M. 1954. The influence of dissolved oxygen concentrations on the toxicity of potassium cyanide to rainbow trout. Journal Exp. Biol., 31:161-164.

Downing (1954) found survival times of rainbow trout in concentrations of potassium cyanide in the range of 0.105-0.155 ppm cyanide increased with an increase in dissolved oxygen concentration between 10% and 100% of air saturation value, the effect being most marked with the lowest concentration of cyanide.

Downing (1954) also determined the rate of increase of survival time with increasing concentration of oxygen did not appear to fall off as air saturation value was approached.

Cairns, John, Jr., Arthur L. Buikema, Jr., Alan G. Heath, and Bruce C. Parker. 1978. Effects of temperature on aquatic organism sensitivity to selected chemicals. Virginia Water Resources Research Center, Virginia Polytechnic Institute. Bull. 106-112:24-71.

Cairns et al. (1978) determined the median lethal concentration of cyanide (CN) to goldfish at 5°C, 15°C, and 30°C to be 3.25 $\pm$ 1.95, 0.44, and 0.28 ppm, respectively.

Cairns et al. (1978) determined the median lethal concentration of cyanide (CN) to golden shiners (Notemigonus crysoleucas) at 5°C, 15°C, and 30°C to be 0.54 $\pm$ 0.19, 0.31 $\pm$ 0.06, and 0.30 $\pm$ 0.08 ppm, respectively.

Cairns et al. (1978) determined the median lethal concentration of cyanide (CN) to bluegill at 5°C, 15°C, and 30°C to be 0.24, 0.16, and 0.19 $\pm$ 0.04 ppm, respectively.

Cairns et al. (1978) found that the toxicity of cyanide to Nitocris, a river snail; Philodina, a rotifer; Daphnia pulex; and Daphnia magna increased as temperature increased but decreased to the oligochaete Aeolosoma.

PHYSIOLOGY

Ruby, Sylvia M., D. George Dixon, and Gerard Leduc. 1979. Inhibition of spermatogenesis in rainbow trout during chronic cyanide poisoning. Arch. Environ. Contam. Toxicol., 8:533-544.

Ruby et al. (1979), in studying testicular tissue of rainbow trout, found that cyanide reduced cell division by about 13% at 0.01 mg/l and 50% at 0.03 mg/l HCN.

Ruby et al. (1979). An additional 9.3% of abnormal mitotic figures (multipolar spindles) were observed at 0.01 mg/l HCN.

Ruby et al. (1979). Tissue from the highest cyanide concentration (0.03 mg/l HCN) revealed extensive necrosis of developing germ cells within their cysts.

Total number of dividing spermatogonia experienced a gradual decrease under the influence of cyanide; the progesssive sequence of cell divisions through the various stages of prophase, metaphase, and anaphase were seriously disturbed by cyanide.

1. Twenty-four percent of total cells were in mitosis in prophase in the control fish as compared to 88% and 55% in trout exposed to 0.01 and 0.03 mg/l HCN, respectively. The high number of cells in prophase should not be interpreted as a stimulating effect of cyanide, but a result of blockage of mitosis beyond prophase causing cells in that stage to accumulate

2. Metaphase was drastically reduced by cyanide, decreasing from 22% in controls to 6% and 12% in trout exposed to 0.01 and 0.03 mg/l HCN, respectively.

3. Cells in anaphase represented 54% of mitotic cells among control fish but the anaphase stage was completely absent from testes of rainbow trout exposed to 0.01 and 0.03 mg/l HCN.

Ruby et al. (1979) found that cyanide decreased the number of spermatogonia in all stages of mitosis with the greatest reduction at the higher concentration tested (0.03 mg/l HCN). Dividing spermatogonia failed to complete mitosis, thus showing that developing germ cells within the testes of fingerling rainbow trout are highly sensitive to the poison, suggesting that cyanide acts as an antimitotic agent which in general affects mitosis.

Ruby et al. (1979) felt that damage or death of spermatogonia due to low concentrations of HCN could result in a significant reduction in the ability of rainbow trout to reproduce.

Doudoroff, Peter. 1956. Some experiments on the toxicity of complex cyanides to fish. Sew. and Ind. Wastes, 28:1020-1040.

Doudoroff (1956). The estimated median tolerance limits ($TL_m$) of sodium cyanide in soft water to P. promelas at 20°C was 0.25, 0.24, and 0.23 ppm as $CN^-$ for 24-, 48-, and 96-hour experiments, respectively.

Doudoroff (1956) determined the $TL_m$ of a mixed solution of sodium cyanide (564 ppm as $CN^-$) and zinc sulfate (394 ppm as Zn) diluted with soft water at 20°C to be 0.20, 0.19, and 0.18 ppm as $CN^-$ during 24-, 48-, and 96-hour experiments, respectively.

Doudoroff (1956) determined the $TL_m$ of a mixed solution of sodium cyanide (439 ppm as $CN^-$) and cadmium sulfate (528 ppm as Cd) diluted with soft water at 20°C to be 0.23, 0.21, and 0.17 ppm cyanide as $CN^-$ for 24-, 48-, and 96-hour experiments, respectively.

Doudoroff (1956) determined a mixed solution of sodium cyanide (600 ppm as $CN^-$) and nickelous sulfate (355 ppm as Ni) diluted with soft water at 20°C to be toxic at all test concentrations above 0.25 ppm as $CN^-$ and felt that cyanide combined with nickel evidently was less toxic than free cyanide.

Doudoroff (1956) found that fish could withstand more than 1,000 times as much cyanide combined with nickel at pH 8.0 than at pH 6.5. A doubling of the hydrogen ion concentration or reduction of pH by little more than 0.3-pH unit can result in more than a 10-fold increase of the toxicity of a mixture of $NaCN\text{-}NiSO_4$.

Leduc, Gerard. 1978. Deleterious effects of cyanide on early life stages of Atlantic salmon (Salmo salar). Journ. Fish. Res. Bd. Canada, 35:166-174.

Leduc (1978) found during incubation of Atlantic salmon eggs in water of 5.4°C that yolk conversion efficiency was reduced at 0.02 mg/l HCN and higher. After hatching, this trend was reversed.

Leduc (1978) determined the sensitivity of Atlantic salmon to cyanide seems to stem from permanent damage caused early in morphogenesis and cell differentiation stages, effects manifested by mortality and congenital defects at very low cyanide levels.

Wilde, C. E., Jr. and R. B. Crawford. 1966. Cellular differentiation in the anamniota. III. Effects of actinomycin O and cyanide on the morphogenesis of fundulus. Experimental Cell Research, 44:471-488.

Wilde and Crawford (1966) found that incubation of mummichog, Fundulus heteroclitus eggs or embryos of all stages in 2 by $10^{-3}$ M NACN reduced oxygen consumption to zero and that embryos in cyanide undergo

normal development patterns during cleavage and blastulation, whereas postblastular development is inhibited. Upon relief of the cyanide inhibition, the embryos renewed their morphogenesis at a normal rate. During cleavage and blastulation, cyanide caused a marked acceleration of glycolysis and had little effect upon the steady-state level of ATP. Glycolysis was not accelerated in postblastular embryos incubated in cyanide while the cyanide inhibitor caused a marked reduction of the level of ATP.

Leduc, Gerard. 1978. Deleterious effects of cyanide on early life stages of Atlantic salmon (Salmo salar). Journ. Fish. Res. Bd. Canada, 35:166-174.

Leduc (1978) determined that cyanide at concentrations as low as 0.01 mg/l HCN produced teratogenic abnormalities in Atlantic salmon (Salmo salar) embryos. He also found Atlantic salmon eggs exposed to 0.1 mg/l HCN became discolored but at 0.01 mg/l HCN there was no difference from control eggs.

BEHAVIOR

Leduc, Gerard. 1978. Deleterious effects of cyanide on early life stages of Atlantic salmon (Salmo salar). Journ. Fish. Res. Bd. Canada, 35:166-174.

Leduc (1978) observed a striking difference between control fish (Atlantic salmon fry) and cyanide-exposed fry at 0.08 and 0.10 mg/l HCN. The controls would swim actively in swarm when disturbed but the poisoned fry remained almost motionless at the bottom.

BIOCONCENTRATIONS

Murachi, Shiro, Nanba Kenji, and Yukio Takeuchi. 1978. Relation between the concentration of cyanide ion detected in carp and that in environmental water. Fac. Fish. Animal Husb., Hiroshima Univ., Fukuyama, Japan. In: Chem. Abstracts, 91:104.

Murachi et al. (1978). Relation between the concentration of cyanide ion detected in carp and that in environmental water. Murachi, Shiro; Nanba, Kenji; Takeuchi, Yukio (Fac. Fish. Anim. Husb., Hiroshima Univ., Fukuyama, Japan). Hiroshima Diagaku Suichikusangakubu Kiyo 1978, 17(2), 199-206 (Japan). The toxicity of cyanide (I) to carp increased with a rise in $H_2O$ temperature. The concentration of I in the blood was higher than that in the hepatopancreas and spleen, or the digestive tract of carp exposed to 10 ppm I solution for five hours. I concentrations in the skin and muscle were higher than that in the viscera of carp which had died in 10 ppm I solution. Thus, I penetrated into the skin and through the gill. I was detectable in the fish washed by running water for 24 hours after death in 5 ppm I solution and also in the fish exposed to 10 ppm I solution for 70 minutes after death from suffocation.

## INVERTEBRATES

### ACUTE EFFECTS

Tatum, William R. 1968. Field observations on the use of sodium cyanide in stream surveys. Tennessee Game and Fish Commission 22nd Annual Meeting of Southern Division of the American Fisheries Society, Oct. 21-23, 1968.

Tatum (1968) found that sodium cyanide reduced the total benthos population by about 77% when applied to a small mountain stream to collect fish.

Cairns, John, Jr., Arthur L. Buikema, Jr., Alan G. Heath, and Bruce C. Parker. 1978. Effects of temperature on aquatic organism sensitivity to selected chemicals. Virginia Water Resources Research Center, Virginia Polytechnic Institute. Bull. 106-112:24-71.

Cairns et al. (1978) determined the 24-hour $LC_{50}$s of KCN to Nitrocris sp. at 5.0°C, 10.0°C, 15.0°C, 20.0°C, and 25.0°C to be 14.0, 13.0, 11.0, 10.0, and 7.6 ppm, respectively.

Cairns et al. (1978) determined the 24-hour $LC_{50}$ of KCN to the rotifer Philodina acuticornis to be 0.50 to 250.0 ppm at a temperature of 20.0°C.

Cairns et al. (1978) determined the 24-hour $LC_{50}$ of KCN to Daphnia pulex at a water temperature of 5.0°C, 10.0°C, 15.0°C, 20.0°C, and 25.0°C to be 0.42, 0.33, 0.32, 0.15, and 0.003 ppm, respectively.

Cairns et al. (1978) determined the 24-hour $LC_{50}$ of KCN to Aeolosoma headleyi, an annelid, at a temperature of 5°C, 10°C, 15°C, 20°C, and 25°C to be 11.0, 100.0, 120.0, 160.0, and 160.0 ppm, respectively.

Cairns et al. (1978) determined the 48-hour $LC_{50}$ of KCN to Nitocris sp. at temperatures of 5°C, 10°C, 15°C, 20°C, and 25°C to be 13.6, 12.8, 10.0, 8.0, and 7.0 ppm, respectively.

Cairns et al. (1978) determined the 48-hour $LC_{50}$ of KCN to Philodina acuticornis at 20°C to be 20.0 to 145.0 ppm.

Cairns et al. (1978) determined the 48-hour $LC_{50}$ of KCN to Daphnia pulex at 5°C, 10°C, 15°C, 20°C, and 25°C to be 0.33, 0.33, 0.18, 0.11, and 0.001 ppm, respectively.

Cairns et al. (1978) determined the 48-hour $LC_{50}$ of KCN to Aeolosoma headleyi at 5°C, 10°C, 15°C, 20°C, and 25°C to be 10.0, 9.0, 120.0, 160.0, and 160.0 ppm, respectively.

# BORON

## FISH

### ACUTE AND CHRONIC

Leclerc, E. 1960. The self-purification of streams and the relationship between chemical and biological tests. In: Proc. 2nd Symp. on Treatment of Waste Waters, P.C.G. Issac (ed.), pp. 281-316, Pergamon Press, London.

Leclerc (1960) found minimum and maximum concentrations of 345.0 mg/l and 380.0 mg/l, respectively, of $Na_2B_4O_7$ to be the incipient lethal level to fish in distilled water with a minimum temperature of 19.0°C.

Alabaster, J. A. 1956. The toxicity of certain weed killers to trout. Proc. 3rd Brit. Weed Contr. Conf., 2:807-808.

Alabaster (1956) determined the $LC_{50}$ for Salmo gairdneri to be 392.0 mg/l $Na_2B_4O_7$ during a 48-hour period with a minimum temperature of 18.0°C. During a 24-hour period the $LC_{50}$ for Salmo gairdneri was determined to be 610.0 mg/l $Na_2B_4O_7$, with a minimum water temperature of 18.0°C.

Wallen, I. E., W. C. Greer, and R. Lasater. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes, 29:695.

Wallen et al. (1957) found a 96-hour $LC_{50}$ of 785.0 mg/l of $Na_2B_4O_7$ for Gambusia affinis in turbid water.

Leclerc, E. 1960. The self-purification of streams and the relationship between chemical and biological tests. In: Proc. 2nd Symp. on Treatment of Waste Waters, P.C.G. Issac (ed.), pp. 281-316, Pergamon Press, London.

Leclerc (1960) found minimum and maximum incipient lethal level concentrations of $Na_2B_4O_7$ to fish to be 805.0 mg/l and 870.0 mg/l, respectively, in hard water with a minimum temperature of 17.0°C.

Wurtz, A. 1945. The action of boric acid on certain fish: trout, roach, rudd. Ann. Sta. Bent. Hydrobiol. Appl. 1, 179; Water Pollut. Res., 20:1653(1947).

Wurtz (1945) observed skin darkening on Salmo gairdneri when exposed to a concentration of 905.0 mg/l of $HBO_3$ in water with minimum and maximum temperatures of 14.0°C and 15.0°C, respectively.

Wallen, I. E., W. C. Greer, and R. Lasater. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes, 29:695.

Wallen et al. (1957) found the 96-hour $LC_{50}$ of $HBO_3$ for Gambusia affinis to be 1,014.0 mg/l in turbid water.

Wurtz, A. 1945. The action of boric acid on certain fish: trout, roach, rudd. Ann. Sta. Bent. Hydrobiol. Appl. 1, 179; Water Pollut. Res., 20:1653(1947).

Wurtz (1945) determined the lethal concentration of $HBO_3$ to Scardinus erythrophthalmus during an 18-hour period to be 1,130.0 mg/l in water with minimum and maximum temperatures of 14.0°C and 15.0°C, respectively. He also found the lethal concentration of $HBO_3$ to Hesperoleucus during a 46-hour period to be 1,130.0 mg/l in water of the same temperature as noted above.

Wallen, I. E., W. C. Greer, and R. Lasater. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes, 29:695.

Wallen et al. (1957) found the 48-hour $LC_{50}$ of $Na_2B_4O_7$ to Gambusia affinis to be 1,790.0 mg/l in turbid water. The 48-hour $LC_{50}$ of $HBO_3$ to G. affinis was 1,900.0 mg/l in turbid water.

Turnbull, H., J. G. DeMann, and R. F. Weston. 1954. Toxicity of various refinery materials to freshwater fish. Symp. on Waste Disposal in the Petrol. Ind., Ind. Eng. Chem., 46:324.

Turnbull et al. (1954) determined the 24-hour $LC_{50}$ of $BF_3$ to Lepomis macrochirus to be 2,380.0 mg/l, with a minimum water temperature of 20.0°C.

Wallen, I. E., W. C. Greer, and R. Lasater. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes, 29:695.

Wallen et al. (1957) found the 24-hour $LC_{50}$ of $Na_2B_4O_7$ to Gambusia affinis to be 2,615.0 mg/l in turbid water.

Leclerc, E. 1960. The self-purification of streams and the relationship between chemical and biological tests. In: Proc. 2nd Symp. on Treatment of Waste Waters, P.C.G. Issac (ed.), pp. 281-316, Pergamon Press, London.

Leclerc (1960) found the minimum and maximum incipient lethal levels of $HBO_3$ to fish in water with a minimum temperature of 20.0°C to be 3,260.0 and 3,530.0 mg/l, respectively.

Wallen, I. E., W. C. Greer, and R. Lasater. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes, 29:695.

Wallen et al. (1957) found the 24-hour $LC_{50}$ of $HBO_3$ to Gambusia affinis in turbid water to be 3,260.0 mg/l.

Wurtz. A. 1945. The action of boric acid on certain fish: trout, roach, rudd. Ann. Sta. Bent. Hydrobiol. Appl. 1, 179; Water Pollut. Res., 20:1653(1947).

Wurtz (1945) found a concentration of 3,620.0 mg/l of $HBO_3$ caused behavioral distress and a concentration of 5,430.0 mg/l $HBO_3$ caused equilibrium loss in Salmo gairdneri in water with minimum and maximum temperatures of 14.0°C and 15.0°C, respectively.

(From EPA Redbook)

Minimum lethal dose for minnows exposed to boric acid at 20°C for six hours reported to be 18,000 to 19,000 mg/l in distilled water and 19,000 to 19,500 mg/l in hard water (Leclerc and Devlaminck, 1955; Leclerc, 1960).

## INVERTEBRATES

### ACUTE

Anderson, B. G. 1946. The toxicity thresholds of various sodium salts determined by the use of Daphnia magna. Sewage Works Journal, 18(1):82-87.

Anderson (1946) found the incipient lethal level of $NABO_3$ to Daphnia magna to be 0.69 mg/l during a 48-hour exposure time in Lake Erie water, with a water temperature of 25.0°C.

Anonymous. 1950. Ohio River Valley Water Sanitation Commission, Subcommittee on Toxicities, Metal Finishing Industries Action Committee. Report No. 3.

Anonymous (1950) found the incipient lethal level of $Na_2B_4O_7$ to Daphnia magna to be 26.0 mg/l.

Jones, J.R.E. 1941. A study of the relative toxicity of anions with Polycelis nigra as test animal. J. Exptl. Biol., 18:170-181.

Jones (1941) found the incipient lethal level of $Na_2B_4O_7$ $H_3BO_4$ to Polycelis nigra during a 48-hour period with a minimum temperature of 14.0°C and a maximum temperature of 18.0°C to be 280.0 mg/l.

## AQUATIC PLANTS

Stanley, R. A. 1974. Toxicity of heavy metals and salts to Eurasian watermilfoil (Myriophyllum spicatum L.) Arch. Environ. Contam. Toxicol., 2:331-341.

Stanley (1974) found that 40.30 mg/l of $B_4O_7$ caused 50% root inhibition in Myriophyllum spicatum during a 32-day exposure period in tap water at a water temperature of 20.0°C.

## MICROORGANISMS

Sheets, W. D. 1957. Toxicity studies of metal-finishing wastes. Sewage Ind. Wastes, 29:1380.

Sheets (1957) observed a 50% reduction of biological oxygen demand in sewage organisms exposed to 87.0 mg/l of $HBO_3$ in buffered water.

SULFIDE

## FISH

## (ACUTE AND CHRONIC)

### EGGS AND HATCHING

Smith, Lloyd L., Jr., Donavon M. Oseid, Gary L. Kimball, and Sayed M. El-Kandelgy. 1976(a). Toxicity of hydrogen sulfide to various life history stages of bluegill (Lepomis macrochirus). Trans. Am. Fish. Soc., 3:442-449.

Smith et al. (1976a) in acute tests found that newly fertilized eggs tested at 5.9 and 6.1 mg/l $O_2$ and 21.9°C hatched in 77 and 66 hours, respectively, with a mean $LC_{50}$ of 0.0218 mg/l $H_2S$.

Smith et al. (1976a) in two chronic tests with durations of 130 and 316 days started with newly fertilized bluegill eggs hatched in $H_2S$ concentrations which varied from 0.0018 to 0.0136 mg/l. Survival decreased to 14% and 11%, with concentration of $H_2S$ increased to 0.0136 and 0.0127 mg/l, respectively.

Adelman, Ira R. and Lloyd L. Smith, Jr. 1970. Effect of hydrogen sulfide on northern pike eggs and sac fry. Trans. Amer. Fish. Soc., 3:501-509.

Adelman and Smith (1970) conducted flow-through bioassays on northern pike eggs (Esox lucius L.) to test the effect of $H_2S$ at two concentrations of oxygen. At an oxygen concentration of approximately 2 ppm mean median tolerance limits ($TL_m$) for eggs were 0.411, 0.076, 0.038, 0.034, and 0.030 ppm $H_2S$ for 24, 48, 72, and 96 hours, and for the duration of the embryonic period, respectively. At an oxygen concentration of approximately 6 ppm median tolerance limits ($TL_m$) were 0.181, 0.046, 0.041, 0.037, and 0.032 ppm $H_2S$ for 24, 48, 72, and 96 hours, and for the duration of the embryonic period, respectively. The pH for each test varied from 7.3-8.0.

Eggs subjected to $H_2S$ resulted in increasing percentages of sac fry with anatomical malformations. At the highest $H_2S$ concentration, 0.061 ppm, 28% of hatched fry were abnormal. Eggs hatched at the lowest $H_2S$ concentrations, 0.004 ppm, produced larger sac fry than controls. Maximum possible safe level of $H_2S$ for eggs is between 0.014 and 0.018 ppm.

Adelman and Smith (1970) determined that $H_2S$ and oxygen acted independently in causing mortality with no significant interaction between the two.

Colby, Peter J. and Lloyd L. Smith, Jr. 1967. Survival of walleye eggs and fry on paper fiber sludge deposits in Rainy River, Minnesota. Trans. Amer. Fish. Soc. 96(3):278-286.

Colby and Smith (1967) found the greatest walleye (Stizostedion vitreum) egg mortality to be over wood-fiber deposits where dissolved sulfide concentrations reached 0.58 ppm within 2 cm of the bottom. They felt that dissolved oxygen, $H_2S$, or $CO_2$ may singularly or in combination account for high egg mortalities over fiber deposits. Eggs and sac fry died within two days when placed on the bottom where the dissolved sulfide concentration was 0.28 ppm. They found walleye eggs are more tolerant of dissolved sulfide when ample dissolved oxygen is present and that dissolved sulfide concentrations of 0.33 and above were toxic to eyed eggs and newly hatched fry.

SAC FRY

Adelman, Ira R. and Lloyd L. Smith, Jr. 1970. Effect of hydrogen sulfide on northern pike eggs and sac fry. Trans. Amer. Fish. Soc., 3:501-509.

Adelman and Smith (1970) conducted bioassays on northern pike (Esox lucius L.) sac fry to test the effect of $H_2S$ at two concentrations of oxygen. The pH varied from 7.3-8.0. Median $TL_m$ values for sac fry were 0.035, 0.016, 0.012, and 0.009 ppm $H_2S$ at 2 ppm oxygen and 0.16, 0.047, 0.030, and 0.026 ppm $H_2S$ at 6 ppm oxygen for 24, 48, 72, and 96 hours, respectively. Sac fry hatched from eggs held at the higher $H_2S$ concentrations were smaller than the controls. Sac fry subjected to $H_2S$ showed decreased growth rates at the higher concentrations. Maximum possible safe level of $H_2S$ for sac fry is between 0.004 and 0.006 ppm for 96-hour exposure. They also found a significant interaction between reduced dissolved oxygen and $H_2S$ in causing mortality of sac fry.

Colby, Peter J. and Lloyd L. Smith, Jr. 1967. Survival of walleye eggs and fry on paper fiber sludge deposits in Rainy River, Minnesota. Trans. Amer. Fish. Soc., 96(3):278-286.

Colby and Smith (1967) determined walleye sac fry are more vulnerable to dissolved sulfide than eggs.

Smith, Lloyd L., Jr., Donavon M. Oseid, Gary L. Kimball, and Sayed M. El-Kandelgy. 1976(a). Toxicity of hydrogen sulfide to various life history stages of bluegill (Lepomis macrochirus). Trans. Am. Fish. Soc., 3:442-449.

Smith et al. (1976a) found that sac fry tested at 21.7°C and 5.8 mg/l $O_2$, four days after egg fertilization, had a 96-hour $LC_{50}$ of greater than 0.0435 mg/l $H_2S$ and at nine days was 0.0253 mg/l $H_2S$.

Smith et al. (1976a) determined that advanced feeding fry tested at 21.8°C and 6.0 mg/l $O_2$, 39 days after egg fertilization, had an $LC_{50}$ at 96 hours of 0.0131 mg/l and after 8 days 0.0128 mg/l $H_2S$.

JUVENILE-ADULT

Hayden, E. P., H. R. Amberg, and R. E. Dimick. 1952. The effect of Kraft mill waste components on certain salmonoid fishes of the Pacific Northwest. Tappi, 35(12):545-549.

Hayden et al. (1952) conducted static bioassays concerning the effects of hydrogen sulfide and sodium sulfide on king salmon (Oncorhynchus tshawytscha), silver salmon (O. kisutch), and coastal cutthroat trout (Salmo clarkii clarkii). Temperatures during tests on king salmon were 17.5°C ± 2°, those with silver salmon were 15°C ± 3°, and with coastal cutthroat trout were 12°C ± 3°; DO levels were from 9-12 ppm. The minimum lethal concentration of hydrogen sulfide for king salmon and cutthroat trout was 1.0 ppm and 1.2 ppm for silver salmon. He found the minimum lethal concentration of sodium sulfide for king salmon to be 3.5 ppm, for silver salmon 3.1 ppm, and cutthroat trout 3.0 ppm.

Wallen, I. E., W. C. Greer, and R. Lasater. 1957. Toxicity to Gambusia affinis of certain pure chemicals in turbid waters. Sewage Ind. Wastes, 29:695.

Wallen et al. (1957) found the 24-, 48-, and 96-hour median tolerance limits of sodium sulfide to Gambusia affinis to be 750 ppm, 750 ppm, and 750 ppm, respectively, with a water temperature of 21-25°C and a pH of 7.6-11.0.

Wallen et al. (1957) found the 24-, 48-, and 96-hour median tolerance limit of sodium sulfite to Gambusia affinis to be 2,600, 2,600, and 2,600 ppm, respectively, with a water temperature of 18-26°C and a pH of 7.1-7.9.

Wallen et al. (1957) found the 96-hour $TL_m$ of ferrous sulfide to G. affinis to be greater than 10,000 ppm at a temperature of 20-26°C and pH of 8.1 to 8.4.

Wallen et al. (1957) found the 96-hour $TL_m$ of ferrous sulfite to G. affinis to be 350 ppm at a temperature of 20-21°C and pH of 3.2-6.9.

Wallen et al. (1957) found the $TL_m$ of ammonium sulfide to Gambusia affinis to be 248 ppm at a water temperature of 21°C and pH of 7.0-8.8.

Wallen et al. (1957) found the $TL_m$ of ammonium sulfite to Gambusia affinis to be 240 ppm at a water temperature of 20-21°C and pH of 2.7-6.7.

Smith, Lloyd L., Jr. and Donavon M. Oseid. 1975. Chronic effects of low levels of hydrogen sulfide on freshwater fish. Progress in Water Technology, 7(3/4):599-605.

Smith and Oseid (1975). Fathead minnow eggs, temperature 24°C, 96-hour $LC_{50}$ of 0.0350 mg/l $H_2S$, and a threshold $LC_{50}$ of 0.0351 mg/l $H_2S$ at 4-8 days.

Chronic Tests - Fish-Bluegills

Smith, Lloyd L., Jr. and Donavon M. Oseid. 1975. Chronic effects of low levels of hydrogen sulfide on freshwater fish. Progress in Water Technology, 7(3/4):599-605.

Smith and Oseid (1975). Young-of-year bluegills after 826 days of exposure as young-of-year to 0.0070 mg/l $H_2S$, their mean weight was approximately 63% of controls.

Smith and Oseid (1975). After 97 days exposure of fish started as adults to levels of hydrogen sulfide up to 0.0078 mg/l there was no appreciable difference from controls except at 0.0014 mg/l where there was a significant increase in growth.

Smith and Oseid (1975). Reproduction (number of eggs per gram of female) was significantly reduced at 0.0007 mg/l $H_2S$ and completely inhibited at 0.0027 and 0.0078 mg/l $H_2S$.

Smith and Oseid (1975). In an experiment started with young-of-year bluegill, no spawning occurred at concentrations of 0.0015 mg/l and higher. This failure of egg deposition appeared to be due to inhibition or absence of spawning behavior since apparently normal numbers of viable eggs were found in ovaries of nonspawning fish.

Smith, Lloyd L., Jr. and Donavon M. Oseid. 1974. Effect of hydrogen sulfide on development and survival of eight freshwater fish species. In: Early Life History of Fish, J.H.S. Blaxter (ed.), 415-430. Springer-Verlag, New York, NY.

Smith and Oseid (1974). Fathead minnows exposed for two reproductive cycles at levels of $H_2S$ between 0.0004 and 0.0069 mg/l and at 23°C during the first cycle had no significant difference in the number of eggs laid per female. In the second cycle, a slight reduction in eggs per female occurred with 912 in a control and 791 at 0.0069 mg/l $H_2S$. Survival of spawning adults was lower in both cycles at the highest concentration (0.0069).

Smith and Oseid (1974). Bluegills held for 826 days had no reproduction at 0.0018 mg/l and significantly reduced fingerling-to-adult survival at 0.0073 mg/l.

Smith and Oseid (1974). Male bluegills during a 46-day test at 0.0014 mg/l $H_2S$ showed a slight alteration in spawning behavior, at 0.0027 mg/l it was greatly reduced, and at 0.0078 mg/l none occurred.

Smith and Oseid (1974). Brook trout held for 37 days prior to spawning (total exposure 76 days) at levels of 0.0055-0.0128 mg/l $H_2S$ deposited fewer eggs per female than controls. At 0.0128 mg/l $H_2S$, the number of eggs laid was 30% of controls and at 0.0055 mg/l was 46%. No apparent effect on behavior was noted at 0.0079 mg/l $H_2S$, but at higher concentrations spawning activity was greatly reduced.

Smith and Oseid (1974). Walleye, fathead minnows, bluegill, rainbow trout, brook trout, northern pike, and goldfish eggs were subjected to various levels of $H_2S$ from 0.005 to 0.059 mg/l to determine effects on incubation.

Smith and Oseid (1974). In egg tests on walleye, percentage hatch dropped from 86% of control at 0.012 mg/l to 9% at 0.159 mg/l, and hatching time was extended from 22 days in the control to 26-27 days at all levels of $H_2S$ treatment.

Smith and Oseid (1974). Survival of eggs incubated at 0.016-0.058 mg/l dropped from 87% at 0.016 mg/l to 17% at 0.058 mg/l. Hatching was extended from 6 days in the control to 8-9 days at the higher $H_2S$ concentrations.

Smith and Oseid (1974). Eggs tested at 0.011-0.035 mg/l survived at 63% of controls in the lowest concentration and 13% in the highest. Hatching time did not vary significantly at the various levels.

Smith and Oseid (1974). Eggs incubated at 0.005-0.011 mg/l $H_2S$ varied from 67% at 0.005 mg/l to 50% at 0.011 mg/l. Brook trout eggs laid by adults held in the same test conditions during maturation and egg deposition had much poorer survival with 45% at 0.007 mg/l and no survival at 0.011 mg/l.

Smith and Oseid (1974). Eggs incubated at 0.006-0.047 mg/l survived at the rate of 76% in the lowest to 4% in the highest concentration.

Smith and Oseid (1974). Eggs incubated at 0.018-0.058 mg/l varied from 88% of controls at the lowest level of $H_2S$ to 6% at the highest.

Smith and Oseid (1974). Eggs held at 0.010-0.029 mg/l hatched at the rate of 95% in the lowest level and 12% in the highest.

Smith, Lloyd L., Jr., D. M. Oseid, and L. M. Olson. 1976(b). Acute and chronic toxicity of hydrogen sulfide to the fathead minnow, Pimephales promelas. Environ. Sci. Technol., 10(6):565-568.

Smith et al. (1976b). Acute toxicity tests of fathead minnows and eggs to hydrogen sulfide.

Smith et al. (1976b). Six bioassays were conducted with fathead minnow eggs at temperatures from 23.8-24.2°C, oxygen from 5.6-6.0 mg/l,

and pH of 7.9 to determine the toxicity of hydrogen sulfide. The 96-hour $LC_{50}$ varied between tests from 0.0291-0.0933 mg/l, with a mean of 0.0536 mg/l $H_2S$. The $LC_{50}$ for the incubation period which ranged from 5-8 days had a mean of 0.0258 mg/l $H_2S$.

Smith et al. (1976b). Tests on fry started within 24 hours of hatching were run at 24°C and 5.4-6.2 mg/l $O_2$. The mean $LC_{50}$ varied from 0.0208 mg/l at 24 hours to 0.0107 mg/l $H_2S$ at 96 hours. Mean LTC at six days was 0.0093 mg/l $H_2S$. $LC_{50}$ at 96 hours varied from 0.0100-0.0115 mg/l $H_2S$ and LTC from 0.0087-0.0101 mg/l $H_2S$.

Smith et al. (1976b). Bioassays were performed on juveniles at six temperatures: 6.5°C, 7.6°C, 10.0°C, 15.0°C, 20.2°C, and 25.0°C. $LC_{50}$ at 96 hours ranged from 0.7754 mg/l at 6.5°C to 0.0423 mg/l $H_2S$ at 25.0°C. The acute toxicity of $H_2S$ to juvenile fish was greatly changed by temperature.

In chronic exposure to $H_2S$ from egg through two generations of laboratory-cultured fathead minnows in flow-through bioassays, adverse effects on growth, survival, and fecundity occurred above 0.004 mg/l $H_2S$. Chronic exposure of wild stock up to 346 days caused adverse effects on growth and survival above 0.008 mg/l $H_2S$.

At comparable temperatures, apparent safe levels with long exposure were 5- to 7-fold lower than the 96-hour $LC_{50}$ for both stocks.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1972. Swimming endurance and resistance to copper and malathion of bluegills treated by long-term exposure to sublethal levels of hydrogen sulfide. Trans. Amer. Fish. Soc., 4:620-625.

Oseid and Smith (1972) found that exposure of bluegill to $H_2S$ increased their resistance to copper. Bluegills conditioned at the lowest $H_2S$ treatment (0.0004 mg/l) had a significantly longer survival time when treated with malathion than controls, but at higher levels of $H_2S$ there was no increased resistance to malathion.

Shelford, Victor E. 1917. An experimental study of the effects of gas waste upon fishes, with especial reference to stream pollution. Bull. Illinois State Laboratory Nat. History, Vol. XI, Article VI, pp. 395-398.

Shelford (1917) found that carbon bisulfide, 0.05 cm per liter of water, intoxicated fish but the fish recovered after 1-1/2 hours in a test in a closed bottle.

Smith, Lloyd L., Jr., Donavon M. Oseid, Gary L. Kimball, and Sayed M. El-Kandelgy. 1976(a). Toxicity of hydrogen sulfide to various life history stages of bluegill (Lepomis macrochirus). Trans. Am. Fish. Soc., 3:442-449.

Smith et al. (1976a) felt that monitoring programs may not be able to detect the lowest levels of $H_2S$ shown to have toxic influence in the laboratory and that any detectable concentration in the field should be considered detrimental to fish production.

Huckabee, John W., C. Phillip Goodyear, and Ronald D. Jones. 1975. Acid rock in the Great Smokies: Unanticipated impact on aquatic biota of road construction in regions of sulfide mineralization. Trans. Am. Fish. Soc., 4:677-684.

Huckabee et al. (1975) found that leaching of sulfide-rich rocks in a mountain stream was responsible for trout and salamander mortalities causing lowered pH to 4.5 and sulfate concentrations as high as 56.0 mg/l; water temperature varied.

Darnell, Reyneat M., Willis E. Pequegnat, Bela M. James, Fred J. Benson, and Richard A. Defenbaugh. 1976. Impacts of construction activities in wetlands of the United States. U.S. EPA Corvallis Environmental Research Laboratory, Corvallis, Oregon. Contract No. 68-01-2452, p. 267.

Darnell et al. (1976) mentioned that construction activities increased hydrogen sulfide levels by increasing sedimentation and burial of organic matter, lowering of the oxygen and the pH of the water, digging and stirring up of bottom sediments, low-level release of water from dams, canalization of coastal marshes, reduction of minimal flow rates and internal circulation patterns, and introduction of sulfides and acids into wetland environments. He (1976) stated that hydrogen sulfide enters aquatic systems from the sediments and eggs and young of fishes and many of the important fish food organisms are apt to be subject to the highest concentrations when stagnant conditions develop.

Adelman, Ira R. and Lloyd L. Smith, Jr. 1972. Toxicity of hydrogen sulfide to goldfish (Carassius auratus) as influenced by temperature, oxygen, and bioassay techniques. Journ. Fish. Res. Bd. Canada, 29(9):1309-1317.

Adelman and Smith (1972) determined the mean 96-hour $TL_{50}$ of hydrogen sulfide to goldfish to be 530 µg/l at 6.5°C to 44 µg/l at 25°C. The log of the $TL_{50}$ increased proportionally to a decrease in the log of temperature.

Adelman and Smith (1972) conducted acute bioassays with hydrogen sulfide at various oxygen concentrations with goldfish. In bioassays without acclimation, the mean $TL_{50}$ was 71 µg/l $H_2S$ at 6.0 mg/l oxygen and 53 µg/l $H_2S$ at 1.5 mg/l oxygen. In tests with acclimation, the mean $TL_{50}$s were 62 and 48 µg/l $H_2S$ at the same oxygen concentrations. In 8 of 10 pairs of tests, the bioassay conducted at the lower oxygen concentration resulted in a lower 96-hour $TL_{50}$. However, the rate of increased toxicity with lowered oxygen is not very great, with the 96-hour $TL_{50}$ reduced only about 26% between oxygen concentrations of 6 and 1 mg/l. Prior acclimation of goldfish to the oxygen concentration of the bioassay had little effect on acute $H_2S$ toxicity except at very low oxygen concentrations.

Chevalier, J. R. 1973. Toxicity of sodium sulfide to common shiners - dynamic bioassay. Tappi, 56(5):135-136.

Chevalier (1973) exposed common shiners (Notropis cornutus Mitchill) to sodium sulfide in concentrations from 0.33 to 3.95 ppm using a dynamic bioassay. Median tolerance limits ($TL_{50}$) were calculated for 24, 48, and 96 hours; results were 2.68, 1.72, and 1.64 ppm, respectively, with a water temperature between 13.0°C and 14.0°C. Most mortality occurred within the first 48 hours.

Smith, Lloyd L., Jr., Donavon M. Oseid, Gary L. Kimball, and Sayed M. El-Kandelgy. 1976(a). Toxicity of hydrogen sulfide to various life history stages of bluegill (Lepomis macrochirus). Trans. Am. Fish. Soc., 3:442-449.

Smith et al. (1976a) ran five tests for 96 hours on juvenile bluegill with a mean size of 3.9 cm; temperatures varied from 20.1°C to 19.9°C with $O_2$ ranging from 5.7 to 6.6 mg/l. The mean 96-hour $LC_{50}$ was 0.0478 mg/l $H_2S$. The $LC_{50}$ of one test run for 8 days to threshold was 0.0491 mg/l $H_2S$ and a second run for 10 days was 0.0468 mg/l.

Smith et al. (1976a) ran seven acute tests on adult bluegill held for 31-174 days prior to bioassay. Mean length of fish was 12.1 cm, temperatures were 19.6°C to 20.3°C, and $O_2$ levels were 4.6 mg/l in one test and in others ranged from 5.8 to 6.4 mg/l. The mean 96-hour $LC_{50}$ was 0.0448 mg/l and showed no relation to $O_2$ levels.

Smith et al. (1976a) tested juvenile bluegill with a $H_2S$ concentration of 0.0092 mg/l and resulted in 100% survival at 717 days and 70% by the 826th day.

Bonn, Edward W. and Billy J. Follis. 1967. Effects of hydrogen sulfide on channel catfish, Ictalurus punctatus. Trans. Amer. Fish. Soc., 96:31-37.

Bonn and Follis (1967) determined at a pH of 7.0 the $TL_m$ of un-ionized hydrogen sulfide was found to be 1.0 ppm for fingerling channel catfish, 1.3 for advanced fingerlings, and 1.4 for adult catfish. This indicates channel catfish have a greater resistance to $H_2S$ with an increase in size or age.

Van Horn, Willis M., J. B. Anderson, and Max Katy. 1949. The effect of Kraft pulp mill wastes on some aquatic organisms. Trans. Amer. Fish. Soc., 79:55-63.

Van Horn, Anderson, and Katy (1949) determined the minimum lethal concentration of $H_2S$ to Lake Emerald (Notropis atherinoides) and spotfin shiners (N. spilopterus) to be 1.0 ppm in a period of 120 hours; temperature equals 18.0°C, pH equals 7.6-7.8, and total alkalinity 140-160 ppm. They determined the minimum lethal concentration of sodium sulfide to the same fish as above to be 3.0 ppm in a period of 120 hours with same temperature, pH, and total alkalinity.

PHYSIOLOGY

Smith, Lloyd L., Jr., Donavon M. Oseid, Gary L. Kimball, and Sayed M. El-Kandelgy. 1976(a). Toxicity of hydrogen sulfide to various life history stages of bluegill (Lepomis macrochirus). Trans. Am. Fish. Soc., 3:442-449.

Smith et al. (1976a) showed that growth rate of bluegill started as eggs and maintained for 316 days exposed to 0.0136 mg/l $H_2S$ had a mean weight of 40.8% of controls. After 113 days of exposure in a second test at 0.0127 mg/l, mean weight was 86.7% of control.

Smith et al. (1976a) in tests started with juvenile bluegill showed a retardation of growth at all $H_2S$ levels tested above 0.0022 mg/l. At 0.0092 mg/l $H_2S$, the mean weight was approximately 85% of the control after 392 days.

Smith et al. (1976a) found in tests with adult bluegills there was no significant decrease in growth at concentrations less than 0.0107 mg/l $H_2S$. The mean weight of fish held for 288 days at 0.0149 mg/l was 59% of control, and in a test running 200 days fish at 0.0144 mg/l $H_2S$ weighed 73% of control.

Smith et al. (1976a) found a significant decrease in food intake (live minnows by immature bluegills) only above 0.0085 mg/l $H_2S$ during a 28-day period. Conversion efficiency ranged from 3.57 in the control to 1.27 at 0.0144 mg/l $H_2S$.

Smith et al. (1976a) in studies on bluegills found when growth rate and long-term survival were used as indices, fish started as eggs were the most sensitive to $H_2S$, whereas fish started as juveniles and adults were less affected.

Smith et al. (1976a) in one test running for 826 days found bluegills failed to spawn in treatments of 0.0022 to 0.0092 mg/l $H_2S$, whereas control fish spawned with an average of 9,928 eggs/female and 130 eggs/g of female. In a second test, prespawning adults, for a period of 97 days, produced 155.5 eggs/g of female in the control, 100.8 eggs/g of female at 0.0010 mg/l, and 51.1 eggs/g of female at 0.0021 mg/l, while a concentration of 0.0041 mg/l $H_2S$ resulted in no egg deposition.

Smith et al. (1976a) determined that a failure to deposit eggs appeared directly related to inhibition of spa ning behavior and that an examination of the gonads in fish which did not spawn did not indicate any apparent malformation or lessening of the number of eggs.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1972. Swimming endurance and resistance to copper and malathion of bluegills treated by long-term exposure to sublethal levels of hydrogen sulfide. Trans. Amer. Fish. Soc., 4:620-625.

Oseid and Smith (1972) found the gross effects of long-term exposure of bluegill to $H_2S$ were reduced growth in the highest concentration (0.0146 mg/l) and progressively increased gill irrigation rate with increased concentrations of $H_2S$.

Oseid and Smith (1972) found that YOY bluegill which had been exposed to higher concentrations of $H_2S$ had a slightly increased capability to endure swimming stress at a concentration of 0.0004 mg/l but that all other swimming tests showed fish to be adversely affected.

Oseid and Smith (1972) found that extended exposure to $H_2S$ levels of 0.0015 mg/l and greater reduced the physical capability of bluegill.

Bonn, Edward W. and Billy J. Follis. 1967. Effects of hydrogen sulfide on channel catfish, Ictalurus punctatus. Trans. Amer. Fish. Soc., 96:31-37.

Bonn and Follis (1967) found when channel catfish were exposed to sublethal concentrations of un-ionized $H_2S$ (concentrations approaching within 0.2 ppm of the $TL_m$ for a given pH) they exhibited nervousness and excessive movement as if attempting to escape the poisonous gas.

Shelford, Victor E. 1917. An experimental study of the effects of gas waste upon fishes, with especial reference to stream pollution. Bull. Illinois State Laboratory Nat. History, Vol. XI, Article VI, pp. 395-398.

Shelford (1917) found that hydrogen sulfide is more toxic to fish when oxygen is low. He found 2 cc per liter fatal to fishes. Water

exposed to the air with 4 cc per liter killed fishes in 18-24 hours. Hardy species of fish lived in 1-1.8 cc per liter without apparent injury.

Terrans, Eugene Leslie. 1980. Acute toxicity of hydrogen sulfide to fish during harvesting operations on commercial catfish farms: Cause, prevention, and cure. Dissertation, University of Oklahoma, pp. 1-123.

Terrans (1980) found that hydrogen sulfide was a competitive inhibitor of cytochrome oxidase in vitro in fathead minnow brain homogenate. A $10^{-6}$ M sulfide concentration increased the $K_m$ of the enzymatic oxidation of cytochrome C from 1.45 times $10^{-5}$ M to 1.00 times $10^{-4}$ M.

Terrans (1980) found that hydrogen sulfide at very low concentrations inhibited cytochrome oxidase in vitro. The inhibition of the enzyme in a channel catfish brain preparation was 18% with $10^{-7}$ M $H_2S$, 64% with $10^{-6}$ M, and 100% with $10^{-4}$ M.

Terrans (1980) found the effect of acute exposure to hydrogen sulfide on the in vivo inhibition of cytochrome oxidase varied with the type of tissue tested. At the point of respiratory arrest, the tissues of the fathead minnow showed cytochrome oxidase activities ranging from control levels in the testes to a 55% inhibition in the kidney. In the channel catfish, the effect ranged from a 28% decrease of the brain cytochrome oxidase activity to a 66% decrease in the heart when fish were sampled at the point of respiratory arrest.

Terrans (1980) found the inhibition of cytochrome oxidase in the channel catfish brain and gill was affected by the un-ionized sulfide concentration.

Terrans (1980). When fish were exposed to a 0.1 mg/l $H_2S$ at 10°C, the cytochrome oxidase of the brain was not affected by even a 30-minute exposure. The enzyme of the gill, however, was inhibited 15% after only 5 minutes and 39% after 30 minutes in the sulfide.

Terrans (1980) found that levels of blood lactate in fingerling channel catfish rose from 11.6 mg/100 ml to 38.1 mg/100 ml when exposed to 0.1 mg/l un-ionized sulfide at a temperature of 20°C.

Terrans (1980) found the inhibition of cytochrome oxidase by hydrogen sulfide is reversible within a short period of time. The enzyme activity of channel catfish brain recovered from a 50% inhibition to control levels within six hours in fresh water at 10°C and at a similar rate at 20°C. At 20°C, the recovery of the enzyme in both the brain and the gill proceeded at the same rate.

Terrans (1980) found that raising the pH from 5.0 to 7.5 reduced the un-ionized sulfide concentration by 84% and decreased the inhibition

of the enzyme in channel catfish by 20%. Apparently any condition that may lower the intramitochondrial pH, such as metabolic acidosis, will increase the toxicity of sulfide.

Terrans (1980) determined the effect of sulfide is increased greatly with increasing temperature. A concentration of 0.5 mg/l $H_2S$ at 10°C was required to produce the same inhibition of enzyme activity in vivo as 0.1 mg/l $H_2S$ at 20°C in studies with channel catfish.

Terrans (1980) found the uptake of sulfide ceased with the onset of respiratory arrest and noted that channel catfish that show severe symptoms of sulfide poisoning during commerical harvesting can be saved if they are removed to fresh water immediately.

## INVERTEBRATES

### ACUTE AND CHRONIC

Anderson, B. G. 1946. The toxicity thresholds of various sodium salts determined by the use of Daphnia magna. Sewage Works Journal, 18(1):82-87.

Anderson (1946) determined the toxicity thresholds of several sodium salts to Daphnia magna. The toxicity of sodium sulfide was 9.4 ppm whenever the toxicity of sodium sulfite was 440 ppm.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1974. Chronic toxicity of hydrogen sulfide to Gammarus pseudolimnaeus. Trans. Amer. Fish. Soc., 4:819-822.

Oseid and Smith (1974) determined the mean 96-hour $LC_{50}$ for Gammarus pseudolimnaeus as 0.022 mg/l of $H_2S$. They indicated that 0.002 mg/l of $H_2S$ is the maximum safe concentration for Gammarus.

Oseid and Smith (1974) did acute tests on Gammarus pseudolimnaeus with hydrogen sulfide concentrations ranging from 0.008 to 0.093 mg/l. Temperature varied from 17.8-18.1°C, oxygen from 5.8-7.4 mg/l, and pH from 7.7-7.9. Total alkalinity ranged from 222-232 mg/l. The total length of organisms exclusive of antennae were 0.7-1.2 cm. For the successive tests, the 96-hour $LC_{50}$s were 0.022, 0.022, 0.024, and 0.021 mg/l $H_2S$. A single threshold test run through 18 days gave an $LC_{50}$ value of 0.011 mg/l $H_2S$.

Oseid and Smith (1974) determined hydrogen sulfide concentration in the four chronic tests with Gammarus pseudolimnaeus varied from 0.0007 to 0.0192 mg/l. Temperatures in three tests varied from 17.1-17.8°C and in one test was 18-18.2°C. Dissolved oxygen ranged from 7.4-8.9 mg/l. Survival at the higher levels was as low as 4% of the control and as high as 57% in another test. The duration of the exposure did not seem to have a direct relationship to the survival totals but the maximum number was assumed to be controlled by chamber size.

Van Horn, Willis M., J. B. Anderson, and Max Katy. 1949. The effect of Kraft pulp mill wastes on some aquatic organisms. Trans. Amer. Fish. Soc., 79:55-63.

Van Horn, Anderson, and Katy (1949) determined the minimum lethal concentration of hydrogen sulfide for Daphnia sp. to be 1.0 ppm, for mayfly larvae of the genus Blasturus and Leptophlebia 1.0, and midge larvae (Chironomus sp.) 750.0 for a period of 48 hours in water with a pH of 7.6-7.8, and total alkalinity of from 140 to 160 ppm.

Van Horn, Anderson, and Katy (1949) determined the minimum lethal concentration of sodium sulfide for Daphnia sp. to be 10.0 ppm, for mayfly larvae of the genus Blasturus and Leptophlebia 1.0 ppm, and midge larvae (Chironomus sp.) 1,000.0 ppm for a period of 48 hours in water of pH 7.6-7.8, with total alkalinity of from 140 to 160 ppm.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1975. Long-term effects of hydrogen sulfide on Hexagenia limbata (Ephemeroptera). Environ. Entomol., 4(1):15-18.

Oseid and Smith (1975) determined the 96-hour $LC_{50}$ of $H_2S$ in acute tests to Hexagenia limbata nymphs to be 0.165 mg/l, with a water temperature of 17.8°C to 18.3°C, dissolved oxygen 4.5 to 6.6 mg/l, and pH of 7.6-7.9.

Smith, Lloyd L., Jr. and Donavon M. Oseid. 1975. Chronic effects of low levels of hydrogen sulfide on freshwater fish. Progress in Water Technology, 7(3/4):599-605.

Smith and Oseid (1975). Gammarus pseudolimnaeus was subjected to subacute levels of hydrogen sulfide of 0.0007-0.0153 mg/l, temperatures of 17.1-17.7°C, and pH of 7.7-7.9 for 65, 95, and 105 days. At the higher levels, there was a marked inhibition of reproduction but at lower levels stimulation or no differences occurred. With concentrations of 0.0128 and 0.0153 mg/l $H_2S$, reproduction did not maintain the original population numbers.

Acute toxicity tests of hydrogen sulfide to Gammarus pseudolimnaeus were conducted at a temperature of 18°C, resulting in a 96-hour $LC_{50}$ mean of 0.0220 mg/l $H_2S$.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1975. Long-term effects of hydrogen sulfide on Hexagenia limbata (Ephemeroptera). Environ. Entomol., 4(1):15-18.

Oseid and Smith (1975) determined the 12-day $LC_{50}$ in acute tests to H. limbata nymphs to be 0.060 mg/l, with same water parameters as above.

Oseid and Smith (1975) in chronic tests of H. limbata, running 138 days with 0.029 mg/l $H_2S$, 37% mortality occurred, and at 0.0762 mg/l, none survived. No subimagos emerged at concentrations of 0.0348 mg/l $H_2S$, but below this level, 30-70% emerged.

Colby, Peter J. and Lloyd L. Smith, Jr. 1967. Survival of walleye eggs and fry on paper fiber sludge deposits in Rainy River, Minnesota. Trans. Amer. Fish. Soc. 96(3):278-286.

Colby and Smith (1967) found that oligochaetes and chironomids were the only groups of bottom organisms frequently found on wood fiber deposits with high sulfide concentrations and oxygen deficiencies.

Colby and Smith (1967) found 16%, 80%, and 88% mortality of Gammarus pseudolimnaeus during 24-, 48-, and 72-hour test periods in dissolved sulfide concentrations of 0.34 ppm.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1974. Chronic toxicity of hydrogen sulfide to Gammarus pseudolimnaeus. Trans. Amer. Fish. Soc., 4:819-822.

Oseid and Smith (1974) showed that in tests conducted on Gammarus pseudolimnaeus with concentrations of $H_2S$ below 0.002 mg/l there was increased reproduction or survival in some tests but there was no consistent effect on mean weight of individuals. At levels in excess of 0.002 mg/l, there was a reduction in numbers and a consequent reduction in total weight of the test group.

Treatments between 0.013 and 0.019 mg/l showed a mean reduction of 71% in numbers and 76% in total weight when compared to the controls.

Oseid, Donavon M. and Lloyd L. Smith, Jr. 1975. Long-term effects of hydrogen sulfide on Hexagenia limbata (Ephemeroptera). Environ. Entomol., 4(1):15-18.

Oseid and Smith (1975) showed in 138-day chronic tests with the nymphal stage of the mayfly Hexagenis limbata mortality was low (0-9%) in all $H_2S$ concentrations lower than 0.0290 mg/l. At 0.0290 mg/l, mortality was 37% and at 0.0762 mg/l $H_2S$, none survived. There was no significant reduction in length of subimagos as the $H_2S$ concentration increased in each experiment. Nymphs exposed to 0.0152 mg/l $H_2S$ were 6% shorter and at 0.0129 and 0.0290 mg/l $H_2S$ were 3% shorter than the controls. The percentage of subimagos emerging varied from 30-75% at levels below 0.0348 mg/l $H_2S$. At this concentration and higher, no emergence occurred.